

Activated carbons from bituminous coals; a comparison of H_3PO_4 and KOH activants

Marit Jagtoyen, Chris Toles and Frank Derbyshire

University of Kentucky Center for Applied Energy Research
3572 Iron Works Pike, Lexington, KY 40511-8433

INTRODUCTION

An earlier study was made of the generation of activated carbons from bituminous coals, using phosphoric acid as a chemical reagent [1-4]. Other work has shown that potassium hydroxide is an effective reagent for the production of high surface area carbons from starting materials such as brown coal [5,6], and other coals, petroleum coke, or mixtures of these [7]. High surface area carbon fibres can also be prepared from charcoal cloth (carbonized viscose rayon cloth) by chemical activation with alkali hydroxides such as KOH at 500°C [8].

For these reasons, the research has been extended to examine the relative effectiveness of H_3PO_4 and KOH as activants for the synthesis of activated carbons from bituminous coal, and the influence of these reagents on reaction mechanisms, porosity development, and adsorptive properties.

EXPERIMENTAL

An Illinois Basin bituminous coal (IBC 106) was supplied by the Illinois Basin Coal Sample Program. Before being used for carbon synthesis, the coal was first ground and cleaned to lower the ash content, using a laboratory scale flotation unit [2]. Properties of the parent and cleaned coals are given in Table 1.

The carbon synthesis procedure has been described in detail elsewhere [2,4]. Briefly, a 20 g sample of dry coal is thoroughly mixed with a given volume of reagent solution at room temperature. The mixture is then reacted first at a low heat treatment temperature (HTT), and subsequently at a higher HTT, in both cases in flowing nitrogen. The solid products are leached with distilled water to pH=6 and vacuum dried at 110°C before further analysis. The tar and oil products are collected in cold traps, and gaseous products are collected in a calibrated graduated gas cylinder.

The conditions normally used with H_3PO_4 were: wt. ratio of acid to dry coal= 0.96, added as 30 cm³ of 50% acid solution; low HTT 170°C for 0.5 to 3h; upper HTT 350 - 650°C for 1h. The corresponding conditions for KOH were: weight ratio=1.42 of KOH to dry coal, added as 28.4 g KOH to 20 g coal in 100 cm³ H₂O; low HTT 75°C for 2h; upper HTT 400 - 900°C for 1h. In some experiments, the reagent to coal ratio was varied. Thermal blank experiments were performed under the same conditions for comparison.

The leached and dried heat treated solids were routinely analyzed for H, C, O, N, S, ash and moisture contents. Fourier transform infrared (FTIR) spectra were obtained from 0.4% loaded KBr discs using a Nicolet 20SX spectrophotometer.

Surface area measurements were obtained from nitrogen adsorption isotherms at 77 K using a Quantachrome Autosorb 6 apparatus. Specific surface areas, S_{BET} , were obtained from the adsorption isotherms using the BET equation. Mesopore surface areas were obtained using the α_s method [9]; standard isotherm data were taken from Rodríguez-Reinoso et al. [10].

RESULTS AND DISCUSSION

Chemical Change

Both reagents promote chemical change at lower temperatures and more extensively than is achieved by thermal reaction. The H/C atomic ratio of carbons produced by different treatments is shown as a function of HTT in Figure 1. In the presence of either activant, dehydrogenation is considerably enhanced [2,4]. Gas analyses have shown that significant quantities of hydrogen may be evolved during chemical activation: for KOH activation up to 70-90% of the parent coal hydrogen is released as H_2 , around 7% with H_3PO_4 treatment, and a negligible amount on thermal treatment. In parallel with these observations, Fourier transform infrared spectroscopy of the carbons shows that chemical activation results in the earlier disappearance of aliphatic absorption bands.

The oxygen content of the carbon products was determined by difference, and hence there is a reasonable margin of error in the data. With this caveat, it seems that the oxygen content of H_3PO_4 carbons falls quickly with HTT, from 12% in the starting coal to about 5% by 350°C, and remains in the range 3-5% between 350 and 650°C. The pattern is different for KOH, where there appears to be an initial reduction in oxygen content, followed by an increase at 400-500°C to values higher than that in the parent coal. Subsequently, the oxygen content is reduced, falling to negligible values at 800 and 900°C. With both reagents, FTIR spectroscopy shows the appearance of carbonyl absorption bands at temperatures from about 75 to 500°C. This band is not evident in the thermal products, and the formation of C=O groups appears to be an intrinsic part of the chemical activation mechanism. Presumably, at high HTT, the carbonyl groups are eliminated by thermal reaction: CO and CO_2 begin to be evolved at HTT over same temperature range where the C=O adsorption bands are reduced in intensity.

Reaction with H_3PO_4 or KOH effects the removal of both inorganic and organic sulfur. Pyritic sulfur is eliminated with relative ease, while some residual organic sulfur remains to high HTT, Figure 2. The mode of sulfur removal is found to depend upon the reagent used: with phosphoric acid, a large proportion of sulfur is liberated as H_2S [1,2,4], whereas with KOH it is released as a water-soluble sulfide during leaching of the heat treated solid, Figure 3. Some sulfatic sulfur is also produced upon KOH activation. Research with model compounds has shown that dibenzothiophene, benzothiophene and thiophenol are desulfurized by reaction with bases, such as KOH, at 375 - 400°C. Ring opening is followed by sulfur removal, probably as a soluble potassium sulfide. Oxygen-containing analogs, indole and benzofuran, also experience ring-opening but no subsequent loss of the heteroatom [11]. Analogous behavior can be anticipated for H_3PO_4 , with the sulfur released as H_2S instead of K_2S .

Porosity

The ratio of reagent to precursor is important to the development of carbon pore structure. As shown in Figure 4, a minimum weight ratio is required to maximize the BET surface area: approximately 0.75 to 1.0 for H_3PO_4 and 1.0 to 1.3 for KOH. At higher ratios, the specific BET surface area decreases. In both series of carbons, there were significant increases in ash content at the highest ratios (9.1% for H_3PO_4 and 11.2% for KOH). It can be concluded that there is no gain to be made from using excess reagent, since it is consumed by reaction with coal mineral matter to form insoluble products [3], and it lowers the surface area per unit mass. If it is assumed that the ash has negligible porosity, then expressing the surface area on an ash-free basis should compensate for this reduction. As shown in the figure, this appears to be the case.

Operating above the minimum ratios, the development of BET surface area is shown as a function of HTT in Figure 5. The two series of chemically activated carbons develop similar surface areas up to HTT of about 500°C. At higher temperatures, the microporosity of the phosphoric acid carbons decreases slightly from a maximum surface area around 840 m^2/g , while that of the KOH-activated carbons continues to increase: at HTT 900°C, the BET surface area approaches 1700 m^2/g . Evidently, the two reagents have quite different temperature dependencies. The thermal products

have negligible accessible surface area, and would have to be subjected to partial gasification in steam or CO_2 to open up the pore structure.

The ash content of the H_3PO_4 carbons increases with temperature from 3.0% at 350°C to 12.0% at 650°C. In contrast to the behavior found with increasing the ratio KOH: coal, the ash content of the KOH carbons decreases with HTT from 6.9% at 400°C to 3.7% at 900°C: a similar observation has been made in related studies [12]. Expressing the data on an ash-free basis, shows that the maximum in the surface area of the H_3PO_4 carbons is flattened, Figure 5. However, the correction does not eliminate the possibility of its existence. Other studies with subbituminous coal, coconut shell and wood precursors [13, 14, 15] have also shown the existence of maxima in surface area at similar HTT. The low ash content of the biomass precursors, and the sharpness of the reported maxima render it unlikely that increases in ash content of the carbons can account for the loss of surface area at high HTT. The more likely causes are considered to be due to the acid becoming inactive for the promotion of further porosity development, and the influence of dimensional contraction of the carbon at high HTT [15].

The mesopore capacities of the chemically activated carbons are low and in the range 20 - 75 m^2/g . For the KOH carbons, there is no clear trend with increasing HTT, whereas that of the H_3PO_4 carbons passes through a shallow maximum at 500-550°C.

It is supposed that, at lower HTT, the chemical reagents promote the formation of crosslinks within the coal structure by ionic mechanisms, leading to the establishment of a rigid, three-dimensional matrix, that is less prone to volatile loss and volume contraction upon heating to higher temperatures. The formation of a crosslinked structure can help to preserve the elements of porosity in the starting material. These suppositions, and the implicit assumption of increased carbon yield have been demonstrated by other work on the phosphoric acid activation of white oak [15]. This more recent work on the activation of white oak has shown that acid treatment actually causes an expansion of the structure that corresponds directly to porosity development. In comparison, extensive shrinkage of the thermal products leads to a collapse of the pore system, making it more difficult to access until carbon is removed by partial gasification.

At high HTT, there is a continuing development of surface area upon KOH activation, and an increase in amount of CO released to the gas phase. On the other hand, with H_3PO_4 treatment, there is clearly no further increase in surface area above about 500°C. It is known that, with increasing temperature, orthophosphoric acid undergoes progressive dehydrogenation [16]. Above about 400°C, extensive polymerization and the elimination of water leads to the formation of metaphosphoric acid $(\text{HPO}_3)_n$. The formation of polyphosphates is also indicated by measurements by ^{31}P NMR and FTIR. This species may be inactive with respect to porosity development, and further increase in HTT above 500°C results in volume contraction accompanied by a reduction in surface area. The same phenomenon could be explained by a structural rearrangement and associated contraction, if the crosslinks formed at low HTT have reached their limit of thermal stability.

Adsorptive properties

The synthesized carbons were subjected to standard test methods to assess their utility [17, 18]. The iodine number provides an indication of the adsorption capacity for small molecules and is usually found to be directly proportional to the BET surface area. The determination was made for a suite of KOH activated carbons, and not surprisingly the highly microporous KOH carbons gave high values for the iodine number.

The methylene blue molecule is much larger than iodine, and its adsorption is restricted mainly to the mesopores. It is a useful indicator of the ability of the carbons to adsorb larger molecules, such as colour bodies from solution. A positive relationship was found between mesopore volume and the methylene blue value for a number of phosphoric acid activated carbons. However, the methylene blue values were low, consistent with the low mesopore surface areas; the values for KOH activated carbons were still lower. It may be concluded that these carbons are not ideally suited for the adsorption of large molecules.

Phenol adsorption capacity can be used to assess a carbon's performance for adsorbing polar compounds. Many of the KOH activated carbons proved to be able to adsorb phenol to a similar extent as a commercial water treatment carbon. The capacity of the acid activated carbons was much less, and disproportionately lower than could be explained by the differences in surface area. Phenol, being a polar molecule, will be attracted to polar sites in the carbon, and it is possible that KOH activation produces carbons with more favorable surface chemistry.

SUMMARY

In the synthesis of activated carbons from bituminous coal using H_3PO_4 and KOH, it is found that both reagents promote chemical change: the removal of hydrogen, oxygen, and organic and inorganic sulfur. Upon KOH activation, up to 70-90% of the parent coal hydrogen can be released as H_2 , and much less upon reaction with H_3PO_4 . Both inorganic and organic sulfur are eliminated; pyritic sulfur removal is relatively facile but some residual organic sulfur remains to high HTT. The mechanism for sulfur removal depends upon the reagent: with phosphoric acid, a large proportion of sulfur is liberated as H_2S and with KOH much is released as a water-soluble sulfide.

The extent of porosity development is found to be influenced by the ratio of reagent to precursor: a minimum ratio is required to maximize the BET surface area. With increasing HTT, the chemically activated carbons develop similar surface areas up to about 500°C. At higher temperatures, the microporosity of the phosphoric acid carbons decreases slightly, while that of the KOH-activated carbons continues to increase. The mesopore capacities of both series of chemically activated carbons are low and in the range 20 - 75 m^2/g . The thermal products have negligible accessible surface area.

The mechanism of chemical activation is considered to involve the formation of crosslinks at low HTT, leading to the establishment of a rigid, three-dimensional matrix, that is less prone to volatile loss and volume contraction upon heating to higher temperatures. The resulting structure can help to preserve the elements of porosity in the starting material. With KOH, there is continuing development of surface area with HTT. With H_3PO_4 treatment, there is no further increase in surface area above about 500°C. This may be due to the formation of inactive species (polyphosphates), or by structural rearrangement and associated contraction, if the crosslinks formed at low HTT have reached their limit of thermal stability.

As they are dominantly microporous, both series of carbons have high adsorptive capacities for small molecules (iodine number), but low capacities for larger molecules (methylene blue value). The KOH carbons have a higher capacity for phenol adsorption than the H_3PO_4 carbons which cannot be explained on the basis of surface area alone. It is suggested that KOH activation produces carbons with more favorable surface chemistry.

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Table 1: Composition of coals.

Coal	Av.P.Diam (μm)	Ash (%)	C	H	N	S	O
			(% daf basis)				
106	80	9.6	83.2	5.5	2.0	3.9	5.4
106clean	5	3.3	84.8	5.5	2.0	2.6	5.1

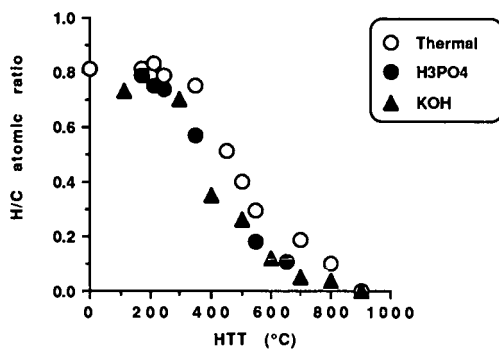


Figure 1: Change in H/C ratio for carbons synthesized from bituminous coals.

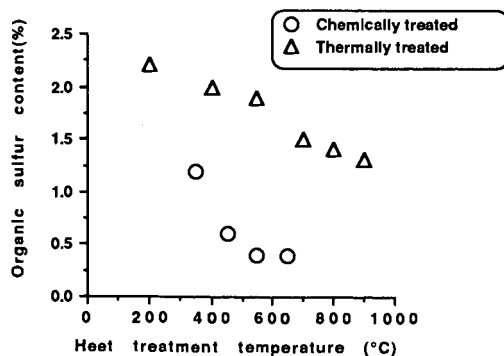


Figure 2: Organic sulfur removal is promoted by chemical treatment.

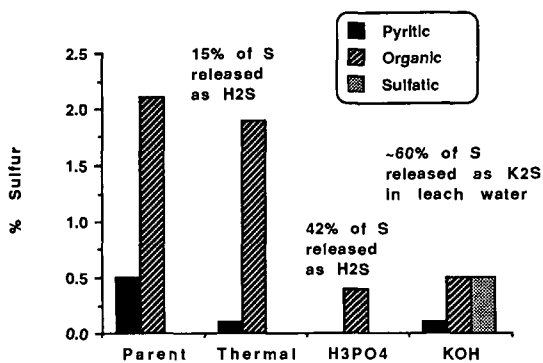


Figure 3: Mode of sulfur removal depends on type of treatment.

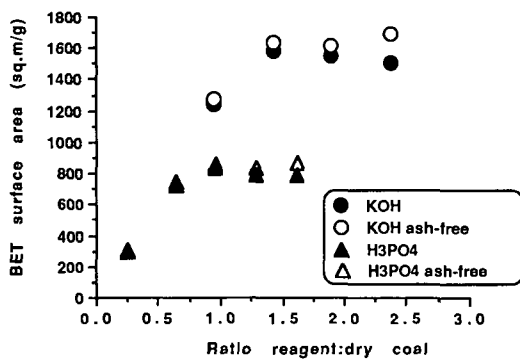


Figure 4: Ratio of reagent to precursor influences surface area (HTT: H₃PO₄, 500C; KOH, 800C)

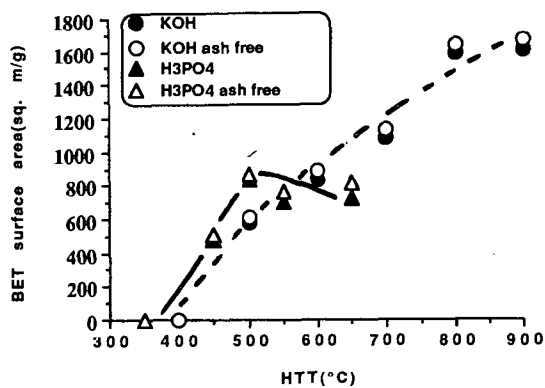


Figure 5: Surface area dependence upon HTT.